

ARCO COKE

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ARCO PETROLEUM PRODUCTS COMPANY
HARVEY TECHNICAL CENTER

Residual Products Research, Development & Technical Services

and

ANACONDA REDUCTION PLANT
COLUMBIA FALLS

PROJECT REPORT

Draft
RAM

Subject: ANODE SHATTER RESEARCH PROGRAM

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to JAK

Summary

A two-level, four-factor factorial experiment was conducted to determine the main and interaction effects of four main variables - coke source, aggregate gradation, % pitch, % QI in pitch - on VSS Soderberg anode properties. While much valuable information was obtained from the factorial experiment, it did not reflect the anode shatter problems encountered in plant anodes. Further investigations in the lab, plus consideration of other facts known about the use of ARCO coke, led to the ultimate explanation of the Columbia Falls anode shatter problem.

It is believed that this problem was triggered by a failure of the rectifier control computer in April, and subsequently propagated by two factors. First, insufficient pitch was being used in the anode paste formulations when ARCO coke was being used plant-wide. Although initial laboratory tests indicated that additional pitch should be used with ARCO coke, operating conditions in the plant led to a gradual reduction of the pitch content over a period of several months. Second, an interaction between the pitch and the de-dust oil ARCO uses to suppress coke dust emissions was discovered. The de-dust oil lowered the viscosity of the pitch, permitting segregation of the pitch in the plastic region of the anodes as they baked to pure carbon. A new plant test at Columbia Falls, using ARCO coke without de-dust oil, has been initiated to test this conclusion in commercial, plant-scale VSS Soderberg anodes.

Background

In mid-January, 1980, a limited plant test of ARCO calcined coke was initiated in fifteen reduction cells at Columbia Falls. Ten cells were charged with 100% ARCO coke anode paste and five control cells with the normal Columbia Falls coke blend (Collier, Martin-Marietta, and Great Lakes Carbon cokes). Five of the ARCO cells received an experimental, CaO-treated pin hole paste as a potential anode stud corrosion inhibitor. On January 30, Columbia Falls began purchasing approximately one-sixth of their calcined coke requirement from ARCO and using it on a plant-wide basis mixed with the normal coke blend. Mixing of the cokes was accomplished by alternately unloading one railcar of ARCO coke with two or more railcars of conventional coke. During February and March generally good anode operating conditions were observed with this ARCO blend coke, although difficulty with control of anode top conditions was reported on many occasions.

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By April 10 the ARCO coke was at the working surface of the test cell anodes, and about six inches from the face of anodes plant-wide. On April 14 the rectifier control computer failed, and manual control of the current to the reduction cells was required. By April 25 the ARCO blend coke was at the face of anodes plant-wide, and increased anode shatter and other anode operating problems were observed. Studies were immediately begun to determine their cause. The rectifier control computer was restored to service on May 7, but the anticipated decrease in anode operating problems was not realized. By May 19 the anode problems had reached serious levels. A detailed study of the problem at Columbia Falls concluded that the rectifier control computer failure had been the triggering mechanism. ARCO coke was also suspect because of the concurrence of its appearance at the face of the anodes with the increased anode shatter. On May 29 Columbia Falls decided to immediately cease using ARCO coke on a plant-wide basis until the cause of the continuing anode problems could be identified and corrected.

Program Outline

Following discussion of the shatter problem at the Anode Technology Committee Meeting on June 3-4, a joint research program between the Harvey Technical Center and Columbia Falls was proposed. During a meeting at CF on June 12, the Anode Shatter Research Program was outlined and immediately initiated. To obtain the most expedient answers and direction for further work, the initial phase of this program was limited to an investigation of the variables having the most probable impact on vertical stud Soderberg anode integrity. Arrangements were also begun for Sumitomo (the Sumitomo Aluminum Smelting Company, Ltd.) to evaluate and compare samples of ARCO and Collier cokes in their laboratories in Tokyo. Finally, a literature search was initiated to determine what, and by whom, similar investigations had been conducted.

To insure the statistical validity of the program, a two-level factorial experiment was developed to determine the main and inter-action effects of the four main variables selected. The four factors, and the "levels" chosen, are as follows:

- 1) Coke Source: ARCO oiled (with de-dust oil) vs. Collier;
- 2) Aggregate Blend: standard Columbia Falls vs. standard Sumitomo;
- 3) % Pitch in anode paste formulation: 27% vs. 30%;
- 4) % QI (quinoline insolubles) in pitch: 12.6% vs. 17.1%.

The Columbia Falls laboratory prepared the sixteen anode paste formulations which contain all combinations of the above four factors at each of their two "levels". The composition, and statistical identity of these formulations is shown in the attached Figure 1. In addition, two formulations were prepared with ARCO dry (no de-dust oil) coke. Analyses were performed, both at CF and HTC, on the raw cokes and pitches, green (unbaked) anode pastes, baked lab test anode specimens, and various samples of anode shatter and anode test cores, as outlined in the attached Table 1.

Results

The as-received screen curves of the raw cokes from ARCO and Collier are shown in Table 2, while the two aggregate gradations (standard Columbia Falls and standard Sumitomo) used are shown in Table 3. Analyses of the raw materials employed in this study are shown in Tables 4-6. Regarding the raw coke analyses, it is believed the low real densities found for Collier and ARCO (oiled) cokes are due to de-dust oil. When coke samples were heated for three hours at 500°C, their respective real densities increased to 2.034 and 2.046. It is proposed that de-dust oil fills some of the pores in the coke, thereby preventing penetration by kerosene in the pycnometer and causing low real density measurements to result.

The variation in L_v values reported by CF and HTC may be due to the different particle sizes used. Columbia Falls used -400 mesh coke while HTC used -200 mesh material. Although degree of crystallinity should be independent of particle size used, it may be that the softer, less crystalline particles are more easily ground when the x-ray samples are being prepared, thereby yielding somewhat different analytical results.

The grindability results are consistent with each other, although they may appear to reflect opposite trends. The Hardgrove grindability test measures the amount of material passing a 200 mesh sieve after the prescribed grinding procedure. The hardness by grinding method measures the amount of material retained on a 100 mesh sieve after grinding. In both cases, the tests indicate ARCO coke to be softer than Collier coke, which is supported by the surface areas and screen curves of the two cokes.

The -200 mesh fines analyses in Table 5 are consistent with the data obtained on the coke aggregates. Under similar grinding conditions, ARCO coke was ground to smaller particles having a larger surface area. ARCO's slightly greater calcination is again reflected by the greater real density and crystallinity of the lab ground fines.

All results reported by Sumitomo substantiate the results obtained at CF and HTC on the raw calcined cokes. In addition, Sumitomo determined that, contrary to Collier, ARCO coke contains no shot coke.

In general, lab tests on the raw coke aggregates and fines suggests that ARCO coke should produce anodes with slightly higher apparent and real densities, require slightly more pitch due to ARCO's greater surface area and smaller particle size, and provide lower carbon consumption and higher metal purity due to lower ash and metals content. SO_x emissions and/or stud corrosion may be greater with ARCO coke due to its higher sulfur content, although this effect was not substantiated in the field test.

Table 6 contains analyses on the two coal tar pitches used in our lab work, plus information Sumitomo provided on the pitch they used. The properties of the Sumitomo pitch were somewhat similar to the Reilly and Koppers pitches, containing 11.5% anthracene insolubles (similar to quinoline insolubles) and 37.1% benzene insolubles (similar to xylene insolubles). Coking values, softening points, and ash contents were nearly identical.

From the green anode paste properties shown in Table 7 we find that ARCO coke consistently yielded lower paste elongations than Collier coke at both pitch concentrations. This would be expected from the surface area, pore size and pore volume, hardness, and screen curves of the two cokes. The consistently higher green apparent density of ARCO pastes is similarly supported by ARCO coke's greater surface area, pore size and volume, and softer texture. The only obvious trend indicated by the TGA results confirms that when using lower %QI pitch, or greater amounts of a given pitch, greater weight losses (volatiles) during heating are observed. Sumitomo's results also indicate the need for an additional 2% pitch with ARCO coke.

The properties of baked test anode specimens are shown in Tables 8-11. As anticipated, the real and apparent densities of baked ARCO specimens are consistently higher than similar samples prepared with Collier coke. The CO₂ reactivity results indicate that ARCO coke anodes should yield less burn-off than Collier anodes. This is supported by ARCO's higher real and apparent densities, which indicate lower microporosity available for CO₂ permeation and attack.

It should be stressed that, in general, all test results indicate that quality anode carbon should be obtained using either coke, either pitch, and either aggregate gradation, providing the proper adjustments are made to the pitch concentration. Once again, the Sumitomo results supported all of our findings. In addition, evaluation of photomicrographs of the green anode pastes and baked test anode specimens revealed no evidence for concern in any of the formulations using any of the raw materials tested.

Due to the few number of anode shatter and anode core samples analyzed, no broad conclusions can be drawn from the data in Table 13. It is significant to note, however, that the core samples indicate a definite lack of homogeneity across all anodes analyzed. This phenomenon is most apparent in the samples taken from pot #935, which was a test cell operating on 100% ARCO coke. The anode in pot #932 was also 100% ARCO coke, #1032 and #1034 were made from ARCO blend coke, and #504 contained no ARCO coke.

Discussion

A preliminary, independent analysis of the data available was conducted by CF and HTC for the Anode Technology Committee meeting. At that time, both facilities came to essentially the same conclusions. First, the data from lab tests did not support actual plant experience. The lab results for both cokes consistently indicated high quality anode carbon with good strength, density, resistivity, and other physical properties. Plant experience, however, showed severe anode shattering and generally poor anode operating conditions throughout the plant. Second, to achieve proper binding and strength in VSS Soderberg anodes, lab results indicated that ARCO coke requires more pitch than Collier coke. This was based on the smaller particle size, larger surface area, and greater microporosity of ARCO coke, plus paste elongation test results obtained

before the limited plant test of ARCO coke was started in mid-January. However, test cell anodes operating on 100% ARCO coke briquets made with the indicated (extra) amount of pitch "wept" pitch over the top of the anode casings. Finally, experience with ARCO coke in other aluminum smelters employing pre-baked anode technology revealed less anode shatter and thermal shock problems with ARCO coke, although they optimally used less pitch with ARCO coke than with their normal cokes.

Columbia Falls then began investigating the difference in %VM between ARCO (oiled) and ARCO (dry) cokes, which was determined to be due to the de-dust oil. Various blends of ARCO de-dust oil (hydrocracker recycle oil) and pitch were prepared and their Brookfield viscosity at 2, 4, 10 and 20 rpm measured. With 1.15% oil in pitch (the same ratio as contained in briquets made with 28% pitch and 72% coke containing 0.45% de-dust oil) the average reduction in pitch viscosity was measured to be nearly 16%. Subsequent analysis of anode core and anode shatter samples revealed a lack of homogeneity of anode carbon in the bake zone: the centers of the anodes were much more porous and weaker than the dense, hard peripheries. While this was true for all anodes examined, it was much more severe in the 100% ARCO coke test cell anodes. Prior testing and inspection had revealed that the tops of the anodes at Columbia Falls are hotter than predicted or desired by Sumitomo. It was also known that the isotherms across CF anodes are severely "hump"-or "loaf"-shaped, rather than flat or slightly curved.

Statistical Analysis

Detailed statistical analysis of the factorial experiment data was performed by two different methods, linear regression and analysis of variance. Several interesting results were obtained, although no unpredictable effects by the four main variables or their first-order interactions were discovered (see Table 14). Of the eight tests which had high correlation coefficients, either the amount of pitch used (3) or the coke source (5) was found to be the most significant factor affecting the test results. % pitch was the most important factor for % elongation and TGA of the green pastes and % porosity of baked test anodes. The elongation and porosity results are obvious, while the TGA results are reasonable: as more pitch is added, more volatiles evolve during baking.

Coke source was the most important factor for all three densities, CO_2 reactivity, and coefficient of thermal expansion. Of particular interest are the latter two, because the results consistently indicate that ARCO coke is superior to Collier coke in these tests. Averaging less than half the CO_2 reactivity of Collier coke test anodes, ARCO coke anodes should have significantly lower carbon consumption due to CO_2 attack. With a nearly 20% lower coefficient of thermal expansion than Collier coke test anodes, ARCO coke anodes should also show less susceptibility to thermal shock and cracking. In practice, both of these benefits have been reported by customers of ARCO coke in aluminum plants using pre-baked anode technology. These results confirmed our belief that the properties of lab-baked test anodes, even though using Soderberg formulations, more closely resemble pre-baked anode processing. Which, in turn, explains why the lab specimens did not reflect the problems encountered in plant anodes.

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Conclusions

Reviewing all of the above facts, the conclusion was reached that the de-dust oil on ARCO coke was aggravating the ability of the pitch to flow to the outsides of the anodes as the briquets melted in the loaf-shaped plastic region of the anodes. Lab results did not lead directly to this conclusion because the lab specimens were baked more like pre-baked than Soderberg anodes, thereby eliminating the opportunity for the pitch to segregate. Supporting this conclusion further are subsequent discussions with several other VSS Soderberg plants, which revealed similar anode problems which were ultimately related to de-dust oil on their calcined coke.

As a result of the work completed to date, some additional lab investigations have been proposed, outlined, and initiated. The Brookfield viscosity measurements will be confirmed and, if possible, kinematic (no external shear) viscosity measurements will be made to more accurately simulate conditions in the anodes. New potential de-dust agents, preferably available from process streams at Cherry Point, will be evaluated. This work will include determining their de-dusting efficiency, effect on pitch properties, and over-all compatibility in aluminum plants and reduction cell anodes. Samples of competitors' de-dust agents have been obtained and will also be evaluated.

More significantly, a new, limited-scale plant test of ARCO calcined coke without any de-dust agent was initiated earlier this month at Columbia Falls. A minimum of 20 reduction cells are being used, ten cells with ARCO (dry) coke and ten control cells with the normal CF coke blend (no ARCO coke). It is anticipated that this new test will confirm our laboratory findings in commercial, plant-scale reduction cells. Also, Columbia Falls is presently evaluating methods of insulating the anode casing side-walls. One effect of this insulation should be to flatten the loaf shape of the bake zone within the anode. If this can be accomplished, the benefits of using ARCO coke (reduced CO₂ reactivity and lower thermal expansion) should become more obvious.

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Figure 1

ANODE SHATTER PROGRAM4-Factor, 2-Level Factorial Experiment

<u>Sample</u>	<u>Trial</u>	<u>Coke</u>	<u>Agg.</u>	<u>% Pitch</u>	<u>% QI</u>
AO-6	(1)	ARCO	CF	27%	12.6%
C-6	a	Collier	CF	27%	12.6%
AO-2	b	ARCO	S	27%	12.6%
C-2	ab	Collier	S	27%	12.6%
AO-7	c	ARCO	CF	30%	12.6%
C-7	ac	Collier	CF	30%	12.6%
AO-3	bc	ARCO	S	30%	12.6%
C-3	abc	Collier	S	30%	12.6%
AO-8	d	ARCO	CF	27%	17.1%
C-8	ad	Collier	CF	27%	17.1%
AO-4	bd	ARCO	S	27%	17.1%
C-4	abd	Collier	S	27%	17.1%
AO-5	cd	ARCO	CF	30%	17.1%
C-5	acd	Collier	CF	30%	17.1%
AO-1	bcd	ARCO	S	30%	17.1%
C-1	abcd	Collier	S	30%	17.1%

		<u>A₀</u>		<u>A₁</u>	
		<u>ARCO COKE</u>		<u>COLLIER COKE</u>	
		<u>B₀</u>	<u>B₁</u>	<u>B₀</u>	<u>B₁</u>
		<u>CF AGG.</u>	<u>S AGG.</u>	<u>CF AGG.</u>	<u>S AGG.</u>
<u>C₀</u> <u>27% PITCH</u>	<u>D₀</u>	(1)	b	a	ab
	<u>12.6% QI</u>	AO-6	AO-2	C-6	C-2
	<u>D₁</u>	d	bd	ad	abd
	<u>17.7% QI</u>	AO-8	AO-4	C-8	C-4
<u>C₁</u> <u>30% PITCH</u>	<u>D₀</u>	c	bc	ac	abc
	<u>12.6% QI</u>	AO-7	AO-3	C-7	C-3
	<u>D₁</u>	cd	bcd	acd	abcd
	<u>17.1% QI</u>	AO-5	AO-1	C-5	C-1

Table 1

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ANODE SHATTER TEST PROGRAM

	<u>Coke</u>	<u>Green Paste</u>	<u>Baked Paste</u>	<u>Anode Shatter</u>	<u>Anode Cores</u>
Real density	HTC/CF		CF	CF	CF
Bulk density	HTC				
Green apparent density		CF			
Baked apparent density			CF	CF	CF
BET surface area (-200 mesh)	HTC/CF				
Particle size distri- bution (-200 mesh)	HTC				
Pore size distribution	HTC				
Cumulative pore volume	HTC				
Porosity			CF	CF	CF
X-ray diffraction (L_c)	HTC/CF				
Full chemical analysis	CF				
TGA		HTC	HTC	HTC	HTC
TMA			HTC	HTC	HTC
CO ₂ reactivity (TGA w/CO ₂)			HTC	HTC	HTC
Optical microscope		HTC	HTC	HTC	HTC
Electron microscope		HTC	HTC	HTC	HTC
Photomicrograph interpretation		HTC/CF	HTC/CF	HTC/CF	HTC/CF
%-elongation		CF			
Resistivity			CF	CF	CF
Compressive strength			CF	CF	CF
Modulus of elasticity			CF	CF	CF
Thermal shock test			HTC		

Table 2

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RAW PETROLEUM COKE SCREEN CURVES

<u>Tyler</u>	<u>Metric</u> (mm)	<u>Collier</u> (wt %)	<u>ARCO Oiled</u> (wt %)	<u>ARCO Dry</u> (wt %)
.371	>9.5	3.60	0.77	3.39
4	>4.75	66.34	20.11	24.48
8	>2.36	25.94	45.40	27.67
14	>1.00	2.53	19.42	19.62
	Coarse	98.41	85.70	75.16
20	>0.850	0.38	5.39	8.56
28	>0.600	0.17	2.71	5.10
48	>0.300	0.27	2.86	5.49
65	>0.212	0.12	0.73	1.51
	Medium	0.94	11.69	20.66
100	>0.150	0.12	0.72	1.12
150	>0.106	0.10	0.55	0.65
200	>0.075	0.10	0.47	0.64
325	>0.045	0.11	0.59	0.64
pan	<0.045	0.22	0.28	1.13
	Fine	0.65	2.61	4.18

Table 3

AGGREGATE BLENDS EMPLOYED

<u>Tyler</u>	<u>Metric</u> (mm)	<u>Anaconda Standard</u> (wt %)		<u>Sumitomo Standard</u> (wt %)	
.371	>9.5	5.0	(14.29)	9.0	(31.58)
4	>4.75	18.0	(51.43)	6.2	(21.75)
8	>2.36	6.0	(17.14)	6.8	(23.86)
14	>1.00	6.0	(17.14)	6.5	(22.81)
	Coarse	35.0	(100.00)	28.5	(100.00)
20	>0.850	2.0	(25.00)	3.0	(19.35)
28	>0.600	2.0	(25.00)	3.0	(19.35)
48	>0.300	1.0	(12.50)	6.5	(41.95)
65	>0.212	3.0	(37.50)	3.0	(19.35)
	Medium	8.0	(100.00)	15.5	(100.00)
100	>0.150	5.0	(8.77)	5.0	(8.93)
150	>0.106	7.0	(12.28)	3.5	(6.25)
200	>0.075	8.0	(14.04)	6.5	(11.61)
325	>0.045	12.0	(21.05)	11.0	(19.64)
pan	<0.045	25.0	(43.86)	30.0	(53.57)
	Fine	57.0	(100.00)	56.0	(100.00)

Table 4

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RAW PETROLEUM COKE ANALYSES

	<u>Collier</u>	<u>ARCO Oiled</u>	<u>ARCO Dry</u>
<u>Real Density</u> (g/cm ³)	2.001	1.990	2.059
<u>Bulk Density, -20+48</u> (lb/ft ³)	56.22	59.17	59.28
<u>BET Surface Area, -4+8</u> (m ² /g)	0.6	0.9	1.3
<u>L_C, X-Ray Diffraction</u> (A) (HTC)	26.9	26.2	28.5
	(CF) 22.3	24.7	23.9
<u>Grindability</u> , Hardgrove	32	35	-
	Hardness by 75.6	58.3	59.1
<u>Volatile Matter</u> (%)	2.729	1.090	0.632
<u>Moisture</u> (%)	0.095	0.170	0.170
<u>Ash</u> (%)	0.48	0.03	0.04
<u>+4 Mesh</u> (%)	69.94	20.88	27.87
<u>Chemical Analysis:</u>			
Sulfur (%)	0.96	2.26	2.18
Vanadium (%)	0.038	0.021	0.020
Iron (%)	0.042	0.010	0.009
Nickel (%)	0.053	0.014	0.013
Silicon (%)	0.031	0.010	0.009
Titanium (%)	0.001	<0.001	<0.001

Table 5

-200 MESH COKE FINES ANALYSES

		Lab Ground ARCO <u>Fines</u>	Lab Ground Collier <u>Fines</u>
<u>Real Density</u> (g/cm³)		2.0552	1.9904
<u>BET Surface Area</u> (m²/g)		5.8	1.7
<u>L_C</u> (A)		26.79	23.82
<u>Microtrac Particle Size Distribution</u> (vol.%)			
212-300 μ	0 %	0 %	
150-212 μ	0	0.9	
106-150 μ	0	2.9	
75-106 μ	5.6	19.3	
58-75 μ	13.5	28.8	
38-58 μ	12.2	21.0	
27-38 μ	9.9	8.6	
19-27 μ	11.3	3.5	
13-19 μ	11.1	4.3	
9.4-13 μ	10.2	2.9	
6.6-9.4 μ	9.4	2.6	
4.7-6.6 μ	7.9	2.9	
3.0-4.7 μ	8.9	2.3	
median μ	28.6	54.0	
<u>Pore Size Distribution</u> (cm³/g)			
<0.1 μ	.020	.012	
0.1-1 μ	.214	.074	
1-10 μ	.355	.454	
10-100 μ	.122	.125	
<u>Cumulative Pore Volume</u> (cm³/g)			
<0.1 μ	.020	.012	
0.1-1 μ	.234	.086	
1-10 μ	.589	.540	
10-100 μ	.711	.665	

Table 6

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RAW COAL TAR PITCH ANALYSES

	<u>Reilly</u>	<u>Koppers</u>	<u>Sumitomo *</u>
<u>Quinoline Insolubles (%)</u>	17.13	12.59	(11.5)**
<u>Xylene Insolubles (%)</u>	34.98	28.82	(37.1)***
<u>Distillation to 360° C (%)</u>	5.8	2.9	-
<u>Ash (%)</u>	0.16	0.12	0.1
<u>Coking Value (%)</u>	56.94	54.77	55.3
<u>Softening Point (° C)</u>	108.0	114.5	111.2
<u>Brookfield Viscosity @ 225°C and 10 R.P.M. (cps)</u>	321.75	178.75	-
<u>Sulfur (%)</u>	0.45	0.68	-

* This pitch was used by Sumitomo in their comparison of ARCO and Collier cokes.

** Anthracene insolubles

*** Benzene insolubles

Table 7

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GREEN ANODE PASTE PROPERTIES

<u>Paste Description</u>	<u>Elongation</u> (%)	<u>Apparent Density</u> (g/cm ³)	<u>TGA</u> <u>in N₂</u> (%)
30% High %QI Pitch			
28.5,15.5,56 Aggregate	13.26	1.596	14.4
Collier Coke	11.22	1.664	15.3
ARCO Oiled Coke			
30% Low %QI Pitch			
28.5,15.5,56 Aggregate	28.19	1.576	16.0
Collier Coke	19.76	1.651	16.0
ARCO Oiled Coke			
27% High %QI Pitch			
28.5,15.5,56 Aggregate	8.77	1.609	13.5
Collier Coke	8.63	1.660	12.0
ARCO Oiled Coke			
27% Low %QI Pitch			
28.5,15.5,56 Aggregate	8.29	1.604	13.8
Collier Coke	6.68	1.660	13.2
ARCO Oiled Coke			
30% High %QI Pitch			
35,8,57 Aggregate	20.30	1.570	15.0
Collier Coke	10.43	1.648	15.1
ARCO Oiled Coke	7.36	1.646	15.1
ARCO Dry Coke			
30% Low %QI Pitch			
35,8,57 Aggregate	29.42	1.573	14.7
Collier Coke	27.43	1.644	16.9
ARCO Oiled Coke			
27% High %QI Pitch			
35,8,57 Aggregate	8.41	1.603	13.3
Collier Coke	4.25	1.642	13.7
ARCO Oiled Coke			
27% Low %QI Pitch			
35,8,57 Aggregate	11.02	1.597	13.0
Collier Coke	7.97	1.641	14.3
ARCO Oiled Coke	5.38	1.614	14.3
ARCO Dry Coke			

Table 8

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BAKED TEST ANODE PROPERTIES

<u>Paste Description</u>	<u>Real Density (g/cm³)</u>	<u>Apparent Density (g/cm³)</u>	<u>Porosity (%)</u>
30% High %QI Pitch			
28.5,15.5,56 Aggregate			
Collier Coke	1.966	1.488	24.31
ARCO Oiled Coke	2.006	1.510	24.73
30% Low %QI Pitch			
28.5,15.5,56 Aggregate			
Collier Coke	1.966	1.471	25.18
ARCO Oiled Coke	2.007	1.501	25.21
27% High %QI Pitch			
28.5,15.5,56 Aggregate			
Collier Coke	1.974	1.476	25.23
ARCO Oiled Coke	2.008	1.523	24.15
27% Low %QI Pitch			
28.5,15.5,56 Aggregate			
Collier Coke	1.973	1.513	23.31
ARCO Oiled Coke	2.004	1.513	24.50
30% High %QI Pitch			
35,8,57 Aggregate			
Collier Coke	1.974	1.486	24.72
ARCO Oiled Coke	2.010	1.497	25.52
ARCO Dry Coke	2.002	1.480	26.07
30% Low %QI Pitch			
35,8,57 Aggregate			
Collier Coke	1.978	1.462	26.09
ARCO Oiled Coke	2.022	1.497	25.96
27% High %QI Pitch			
35,8,57 Aggregate			
Collier Coke	1.977	1.505	23.87
ARCO Oiled Coke	2.005	1.520	24.19
27% Low %QI Pitch			
35,8,57 Aggregate			
Collier Coke	1.983	1.482	25.26
ARCO Oiled Coke	2.010	1.517	24.53
ARCO Dry Coke	2.005	1.474	26.48

Table 9

15

BAKED TEST ANODE PROPERTIES

<u>Paste Description</u>	<u>Compressive Strength (lb/in)</u>	<u>Modulus of Elasticity (x10⁵ lb/in²)</u>
30% High %QI Pitch		
28.5,15.5,56 Aggregate		7.0
Collier Coke	5825	
ARCO Oiled Coke	5814	6.8
30% Low %QI Pitch		
28.5,15.5,56 Aggregate		5.2
Collier Coke	5520	
ARCO Oiled Coke	5768	5.2
27% High %QI Pitch		
28.5,15.5,56 Aggregate		4.9
Collier Coke	5879	
ARCO Oiled Coke	6131	7.2
27% Low %QI Pitch		
28.5,15.5,56 Aggregate		5.3
Collier Coke	6474	
ARCO Oiled Coke	6026	5.5
30% High %QI Pitch		
35,8,57 Aggregate		4.5
Collier Coke	6069	
ARCO Oiled Coke	5263	5.3
ARCO Dry Coke	5254	6.6
30% Low %QI Pitch		
35,8,57 Aggregate		6.1
Collier Coke	5782	
ARCO Oiled Coke	5697	5.6
27% High %QI Pitch		
35,8,57 Aggregate		8.2
Collier Coke	6343	
ARCO Oiled Coke	5970	5.6
27% Low %QI Pitch		
35,8,57 Aggregate		4.5
Collier Coke	5422	
ARCO Oiled Coke	5831	5.4
ARCO Dry Coke	4619	5.8

Table 10

16

BAKED TEST ANODE PROPERTIES

<u>Paste Description</u>	<u>Electrical Resistivity</u> (ohm-in)	<u>Malleability</u> (%)
30% High %QI Pitch		
28.5,15.5,56 Aggregate		
Collier Coke	0.0030	0.76
ARCO Oiled Coke	0.0032	0.80
30% Low %QI Pitch		
28.5,15.5,56 Aggregate		
Collier Coke	0.0029	1.01
ARCO Oiled Coke	0.0031	1.09
27% High %QI Pitch		
28.5,15.5,56 Aggregate		
Collier Coke	0.0032	1.11
ARCO Oiled Coke	0.0031	0.77
27% Low %QI Pitch		
28.5,15.5,56 Aggregate		
Collier Coke	0.0030	1.13
ARCO Oiled Coke	0.0031	0.97
30% High %QI Pitch		
35,8,57 Aggregate		
Collier Coke	0.0032	1.25
ARCO Oiled Coke	0.0031	0.87
ARCO Dry Coke	0.0033	0.69
30% Low %QI Pitch		
35,8,57 Aggregate		
Collier Coke	0.0031	0.85
ARCO Oiled Coke	0.0029	0.90
27% High %QI Pitch		
35,8,57 Aggregate		
Collier Coke	0.0029	0.63
ARCO Oiled Coke	0.0031	0.98
27% Low %QI Pitch		
35,8,57 Aggregate		
Collier Coke	0.0032	1.09
ARCO Oiled Coke	0.0028	0.97
ARCO Dry Coke	0.0031	0.69

Table 11

17

BAKED TEST ANODE PROPERTIES

<u>Paste Description</u>	<u>CO₂ Reactivity (by TGA) (x 10⁻⁶ mg/ min/°C/cm²)</u>	<u>Coefficient of Thermal Expansion (by TMA) (x 10⁻⁶/°C)</u>		
		<u>@ 50°C</u>	<u>@ 600°C</u>	<u>Avg.</u>
30% High %QI Pitch				
28.5,15.5,56 Aggregate	7.18	3.23	5.55	4.58
Collier Coke	4.57	2.26	4.57	3.68
ARCO Oiled Coke				
30% Low %QI Pitch				
28.5,15.5,56 Aggregate	6.70	3.56	6.20	4.99
Collier Coke	4.01	2.82	4.75	3.93
ARCO Oiled Coke				
27% High %QI Pitch				
28.5,15.5,56 Aggregate	7.70	2.46	5.51	4.37
Collier Coke	3.91	2.43	4.88	3.76
ARCO Oiled Coke				
27% Low %QI Pitch				
28.5,15.5,56 Aggregate	8.91	2.46	5.26	4.17
Collier Coke	3.41	1.67	4.09	3.43
ARCO Oiled Coke				
30% High %QI Pitch				
35,8,57 Aggregate	8.17	3.05	5.96	4.89
Collier Coke	3.58	1.96	4.25	3.46
ARCO Oiled Coke	3.55	2.25	4.51	3.74
ARCO Dry Coke				
30% Low %QI Pitch				
35,8,57 Aggregate	7.59	1.94	5.83	4.15
Collier Coke	3.68	2.14	4.68	3.82
ARCO Oiled Coke				
27% High %QI Pitch				
35,8,57 Aggregate	8.50	1.91	5.11	4.44
Collier Coke	4.39	1.93	3.90	3.51
ARCO Oiled Coke				
27% Low %QI Pitch				
35,8,57 Aggregate	8.32	3.39	5.52	4.68
Collier Coke	3.16	1.98	4.96	3.91
ARCO Oiled Coke	2.96	2.32	4.74	4.04
ARCO Dry Coke				

NOTE: No weight change was observed running TGA under N₂.

Table 12

SUMMARY OF SUMITOMO RESULTS

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Coke Quality

	<u>ARCO</u>	<u>Collier</u>
<u>Real Density</u> (g/cm ³)	2.024	1.979
<u>Bulk Density, -20+48</u> (lb/ft ³)	56.19	58.06
<u>Grindability, modified Hardgrove</u> (%)	32.5	29.5
<u>Volatile Matter</u> (%)	0.35	0.60
<u>Sulfur</u> (%)	2.51	1.08
<u>Electrical Resistivity, -65+100</u> (ohm-in)	0.0344	0.0433
<u>Shot Coke, +.371</u> (%)	0	8.4
<u>-.371+4</u> (%)	0	4.0

Paste Quality

<u>Pitch required for 15% elongation</u> (%)	30.	28.
<u>Apparent Density, 28% pitch</u> (g/cm ³) (220°C)	1.11	1.37
(500°C)	1.17	1.31
(900°C)	1.16	1.31
<u>30% pitch</u> (g/cm ³) (220°C)	1.44	1.18
(500°C)	1.35	1.29
(900°C)	1.34	1.28

Baked Test Anode Quality (@ optimum % pitch)

<u>Real Density</u> (g/cm ³)	2.006	1.983
<u>Apparent Density</u> (g/cm ³)	1.375	1.356
<u>Porosity</u> (%)	31.5	31.6
<u>Electrical Resistivity</u> (ohm-in)	0.0032	0.0033
<u>Compressive Strength</u> (lb/in ²)	3769	3485
<u>Bending Strength</u> (Kg/cm ²)	75	65
<u>CO₂ Reactivity</u> (mg/cm ²) (950°C)	1.4	2.3
(1000°C)	3.4	4.3
<u>Thermal Shrinkage @ 500°C</u> (%)	-1.4	-1.6

Table 13

ANODE SHATTER AND ANODE CORE PROPERTIES

	<u>Anode Shatter</u>		<u>Anode Cores</u>			
	<u>#932</u>	<u>#1034</u>	<u>#935</u>	<u>#1032</u>	<u>#504</u>	
			<u>outside</u>	<u>between</u>	<u>outside</u>	<u>center</u>
				<u>center</u>		
<u>Real Density</u> (g/cm ³)	-	1.99	2.03	2.03	1.97	2.02
<u>Apparent Density</u> (g/cm ³)	-	1.58	1.63	1.52	1.67	1.47
<u>Porosity (%)</u>	-	20.4	19.7	25.1	15.5	27.2
<u>Elec. Resistivity</u> (ohm-in)	-	.0029	.0030	.0030	.0027	.0030
<u>Compressive Strength</u> (lb/in ²)	-	5134	6257	5271	6225	4427
<u>Modulus of Elasticity</u> (x10 ⁵ lb/in ²)	-	4.0	5.7	5.7	5.1	6.3
<u>Malleability (%)</u>	-	-	1.01	0.90	-	0.65
<u>Flexural Strength</u> (Kg/cm ²)	-	-	221.5	184.2	180.0	-
<u>CO₂ Reactivity</u> (x 10 ⁻⁶ mg/min/°C/cm ²)	3.81	4.70	3.92	-	6.55	5.80
<u>Coefficient (at 50°C)</u>	3.30	2.59	2.09	2.18	1.99	2.73
<u>of Thermal (at 600°C)</u>	7.16	4.67	4.26	5.54	3.98	4.88
<u>Expansion (Average)</u> (x 10 ⁻⁶ /°C)	6.62	4.42	3.61	3.80	3.52	4.42

NOTE: No weight change was observed running TGA under N₂.

Table 14

ANODE SHATTER RESEARCH PROGRAM

MAIN & INTERACTION EFFECTS BY ANALYSIS OF VARIANCE

Variable(s)	Green Anode Paste			BAKED TEST ANODES				
	% Elongation	Apparent Density	TGA in N ₂	Real Density	Apparent Density	% Porosity	CO ₂ Reactivity	Coefficient of Thermal Expansion
Coke Source	4	1		1	1		1	1
Aggregate Blend		2		2				
% Binder Pitch	1		1		2	1		
% QI in Pitch	2	4		4				
Coke - Aggregate								
Coke - % Pitch		3		3				
Coke - % QI								
Aggregate - % Pitch				5				
Aggregate - % QI				4				
% Pitch - % QI	3							
Test Prediction	Pitch Conc.	Wetting Mixing	Baking Process		Carbon Consumption			Anode Expansion

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